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## METHODS OF MEASURING THE RHEOLOGICAL PROPERTIES OF COMPOUNDS FOR EXTRUSION

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A classification is given for methods of measuring the rheological properties of ceramic compounds for extrusion. Depending on the magnitude of the shear stresses under which the testing is performed, it is proposed that the methods of investigation be divided into structural-mechanical and rheological. The most informative methods as well as the structural-mechanical and rheological parameters obtained with these measurements are described. Recommendations are given for using each method for scientific investigations and for checking the parameters of the molding compounds in the production of extruded ceramic articles.

**Key words:** ceramic mixes, extrusion, rheological properties, methods of measurement.

Extrusion is often used to form many products, including ceramic (building materials, catalysts, and so on). The relation between the rheological properties and other aspects of the extrusion technology can be represented by a diagram (Fig. 1), showing graphically the importance of rheology as a science.

An important component of successful extrusion molding is a definite combination of rheological properties of the compounds [1 – 3]:

developed plasticity, making it possible to impart the required shape to the compound;

the required yield point, making it possible to preserve the shape and dimensions of the green extrudate at subsequent technological stages;

sufficiently strong coagulation structure of the compound, making it possible to maintain the rheological properties in an acceptable range directly in the molding machine under the action of high shear stresses (specifically, thixotropic lowering of the viscosity should not result in a transition of the compound into a flow regime with minimal viscosity).

The methods for studying the rheological properties of compounds can be divide into two basic categories [4]:

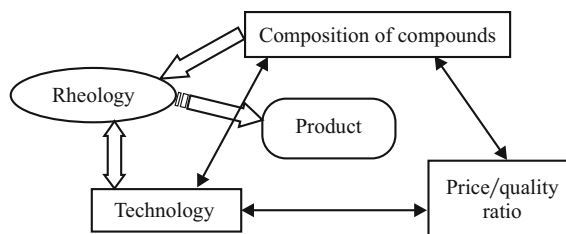
1) direct testing measurements, giving information on the physic-chemical, mechanical and technological properties of compounds [1, 5 – 7];

2) analytical methods which, using mathematical models, make it possible to calculate the flow of compounds [8, 9].

The first group is hugely popular with and trusted by researchers – practitioners, since the rheological parameters are obtained directly from the experimental data. Before proceeding to an analysis of the main methods, it is necessary to point out that molding compounds for extrusion are classified as solid-like viscoplastic bodies, i.e., depending on the external conditions of the actions they act as a solid substance as well as a liquid [1, 5, 6, 10, 11]. With such rheological behavior the corresponding requirements are imposed on the methods used to measure the properties of compounds, i.e., the following parameters must be measured with their help:

parameters characterizing a solid body;  
parameters characterizing plasticity;  
in a large interval of shear stresses or rates.

Rheological methods can be divided into integral (determination of the total effect of a flow) and differential (observation of the deformations in time as each point of the dispersed system during its flow) [5 – 7, 10 – 12]. Likewise, instruments are divided into instruments with uniform and nonuniform stress field. The former include rotational vis-



**Fig. 1.** Interrelation of the rheological properties and other aspects of extrusion technology.

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cometers and instruments with translation of the working organ; the latter into capillary viscosimeters and instruments based on the method of vibrations [7, 12].

The existing methods can be divided according to the method of measurement [1]:

rotational viscosimetry (records the parameters of the rotation of the working organ of the instrument, touching the system being tested) [4, 7, 11 – 13];

capillary viscosimetry (measurement of the flow time of a material through a capillary with a known cross section) [4, 12, 14];

instruments with a plane-parallel gap (measurement of the development of tangential displacement in time) [4, 5, 6, 15];

penetration methods (penetration of the working organ, for example a cone or stamp, into the compound being tested) [5, 6, 15 – 17];

other methods (pendulum, vibration, flow spreading, viscosimeters with sinking or up-floating all, and so forth) [7, 11, 18].

Because of the great diversity of types of instruments it is difficult to delimit their regions of application. Most instruments were developed for performing rapid testing. They are convenient for monitoring the rheological properties directly during production and are quite simple to use [4, 7, 13, 16, 17]. In what follows only the methods which make it possible to obtain parameters of compounds that have an unequivocal physical interpretation will be examined.

The instruments for measuring the properties of compounds can also be classified according to the following features:

- 1) measurement of resilient-elastic and plastic properties under shear stresses, close to the limit of flow (plastometers);
- 2) measurement of properties of pastes in the regime of developed flow (viscosimeters).

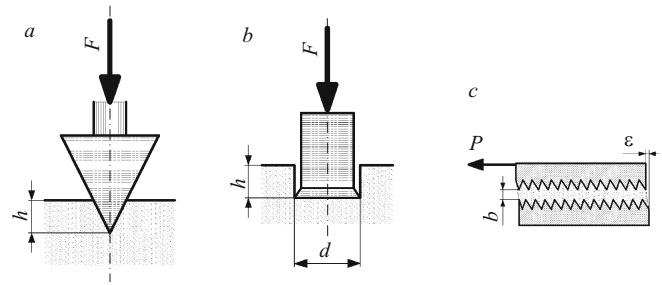
In accordance with this classification, we shall call the parameters obtained using instruments of the first type structural mechanical properties and using instruments of the second type rheological properties.

## METHODS OF MEASURING STRUCTURAL-MECHANICAL PROPERTIES

*P. A. Rebinder's Conical Plastometer* [5, 6]. The plastometer is characterized as an instrument with a uniform stress field, a penetration instrument. The principle of operation of this instrument is based on measurement of the penetration depth of a cone into the compound under a fixed external load (Fig. 2a). Given an external load  $F$  and measuring the penetration depth  $h$  of a cone it is possible to calculate the plastic strength  $P_m$  of the compound being tested [1, 5, 17, 18]:

$$P_m = K_\alpha F/h^2, \quad (1)$$

where  $K_\alpha$  is a dimensionless coefficient that depends on the vertex angle of the cone.



**Fig. 2.** Principle of operation of a conical plastometer with P. A. Rebinder's construction (a), stamp with a constant cross section (b), and D. M. Tolstoi's plastometer with parallel movement of a plate construction (c).

*Stamp with a Constant Cross Section* [16]. This method is based on pressing into the system being tested a stamp with a constant cross section under a known load (Fig. 2b) and is a penetration method. When the stamp is pressed in, compression and shear stresses develop in the material. The character of the development of the deformations in this case makes it possible to model to a known degree the character of the deformations which the molding compound undergoes in the process of extrusion. The relation between the load and the relative deformation can be expressed by the equation

$$L\varepsilon' = \left( \frac{p + P_c}{P_s - p} \frac{P_s}{P_c} \right),$$

where  $L$  is the coefficient of dislocations, which characterizes the change of the structure of the compound during deformation;  $\varepsilon'$  is the relative deformation, equal to the ratio of the absolute deformation  $h$  to the thickness of the deformed layer, taken as being equal to the diameter  $d$  of the stamp;  $p$  is the pressure per unit area of the stamp during tests, Pa;  $P_c$  is the stress corresponding to the initial compaction of the sample; and,  $P_s$  is the stress under which the sample is destroyed.

The dependence of the relative deformation on the external pressure has an inflection that corresponds to the limit of compression under the deformation conditions adopted:

$$p = (P_s - P_c)/2 = P_m. \quad (2)$$

The inflection point separates the section where compression predominates from the section where shear predominates.

An empirical constant  $R_m$ , called the coefficient of moldability [16], was proposed to make a comparative determination of the moldability of compounds according to the results of tests performed using a stamp with constant cross section:

$$R_m = L(1 - E_1/E_2) \times 0.1,$$

where  $E_1$  and  $E_2$  are the elastic modulus and the shear modulus, respectively.

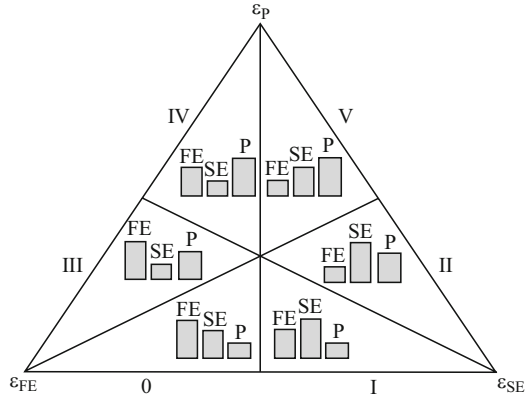


Fig. 3. Diagram of the development of deformation in solid-like viscoplastic disperse systems.

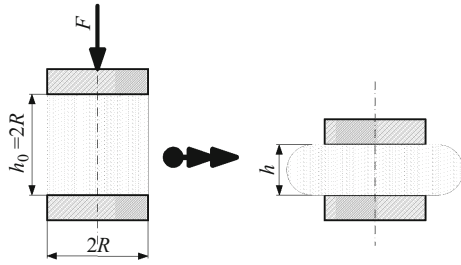


Fig. 4. Principle of action of a plastometer with parallel plates.

*D. M. Tolstoi's Plastometer with Parallel-Moving Plate Construction* [5, 6]. Uniform shear deformations develop in the plastometer under a tangential load (Fig. 2c). The result of the measurements is a set of curves of the development of deformations in time. The process of deformation development is described satisfactorily by the Maxwell – Shvedov and Kelvin model [1, 6, 9, 15]

$$\varepsilon' = \frac{P}{E_1} + \frac{P}{E_2} \left[ 1 - \exp\left(-\frac{E_2 \tau}{\eta_2}\right) \right] + \frac{(P - P_{k1}) \tau}{\eta_1}, \quad (3)$$

where  $\varepsilon'$  is the relative deformation under constant load  $P$ ;  $\tau$  is the time during which the load acts with  $P = \text{const}$ ;  $\eta_1$  and  $\eta_2$  are the highest and lowest plastic viscosity, respectively; and,  $P_{k1}$  is the maximum shear stress.

The reduced deformations can be calculated from the model (3): elastic  $\varepsilon_{FE}$  (fast elastic), elastic  $\varepsilon_{SE}$  (slow elastic), and plastic  $\varepsilon_P$ . According to S. P. Nichiporenko [19], these deformations of disperse systems can be divided into six structural-mechanical types according to their ratio (Fig. 3). The indicated constants can be used to calculate the structural-mechanical characteristics:

$\Pi_s = P_{k1} / \eta_1$  is the static plasticity characterizing the rate of development of plastic deformations;

$\lambda = E_2 / (E_1 + E_2)$  is the elasticity showing the fraction of the slow elasticity in the reverse deformation process;

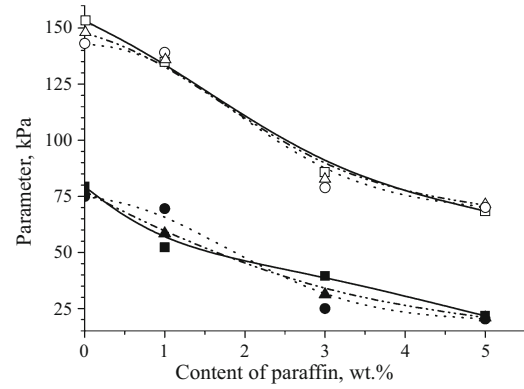


Fig. 5. Values of some structural – mechanical constants for molding pastes: ■, □) maximum shear stress, Eq. (3); ●, ○) maximum compression stress, Eq. (2); ▲, △) plastic strength, Eq. (1).

$\Theta = \eta_1 / E$  is the relaxation period, showing the time over which the fast – slow elastic deformations decrease by a factor of  $e = 2.71, \dots, n$ , transforming into the plastic deformations ( $E = (E_1 + E_2) / E_1 E_3$ ) — equilibrium modulus).

*Plastometer with Parallel Plates* [20]. The method consists in compressing a cylindrical sample (Fig. 4) under a fixed load

$$P = Fh / (\pi R^3).$$

The plastic flow regime ( $0.3 < h/R < 0.8$ ) can be described by the linear equation [4]:

$$P = 2/3 K_1 + \alpha K_2 (h/R),$$

where  $\alpha$  is a coefficient that depended on the surface of the plate (smooth or fluted);  $K_1$  is the maximum friction;  $K_2$  is the maximum plasticity; and,  $R$  is the radius of the sample.

Thus, tests performed on compounds by the methods examined above permit obtaining an adequate set of structural-mechanical parameters characterizing the system as solid or plastic body in the range of shear stresses for which a flow regime with the maximum friction (Shvedov creep [5, 6, 10, 15]). At the same time a critical analysis shows that the same parameter obtained using different instruments has a different name. Figure 5 shows the values of the plastic strength, the yield point, and the maximum shear stress of measured for compounds based on  $\text{Al}(\text{OH})_3$  and  $\gamma\text{-Al}_2\text{O}_3$  [21]. It is evident that the values presented are close and fall within the error range of the methods. This is explained by the fact that the parameters in Fig. 4 have the same physical meaning — the stress at which plastic flow of the compound starts, i.e. the yield stress of the compound.

The conical plastometer is best used for rapid checking of compounds. For example, the moisture content of a compound can be determined according to the value of the plastic strength [1, 6, 15, 17]. A stamp with a constant cross section is suitable for studying compounds which have a short induction period, for example, molding compounds containing ce-

ment [1, 16, 21]. A plastometer with parallel plates can be used for such purposes [4]. D. M. Tolstoi's plastometer gives the most complete information on the structural-mechanical properties, but it has limitations in use: the compound must retain its properties (crystalline bonds should not be formed) for at least one day, which is necessary in order to perform correct tests; the yield point must be adequate to prevent plastic deformation of a compound under the weight of the top plate (see Fig. 2c).

## METHODS OF MEASURING THE RHEOLOGICAL PROPERTIES

*Rotational viscosimetry* makes it possible to obtain the values of the stress and shear rate as well as the effective viscosity in terms of the corresponding physical quantities [1, 4, 7–9]. Rheometers making possible to perform these measurements are said to be absolute or viscosimeters [4]. Rheometers differ by, first and foremost, the geometry of the measuring cells (Fig. 6). Only shear deformations develop in cylinder–cylinder, hemisphere–hemisphere, and cone–cone rheometers; shear together with compression is observed in disk–disk, disk–ring, and disk–cone rheometers [7, 12]. The cone–cone and disk–disk measuring pairs are characterized by a nonuniform stress field; all others are characterized by a uniform stress field. We note that each viscosimeter functions in a definite range of the effective viscosity. The cells shown in Fig. 6d, e, and f are suitable for investigating the rheological properties of compounds to be used for extrusion.

Two basic variants of the operation of the measuring cells are used in absolute rheometers [7]:

- rheometer with controllable stress (CS); the shear stress is set and the deformation rate is measured;
- rheometers/viscosimeters with controllable shear rate (SR); the shear rate is set and the shear stress is measured:

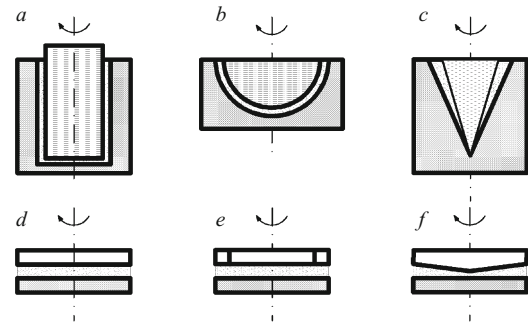
*Searle measuring system:* a rotor rotates; the rotational moment is measured on the axis of the rotor; outer cylinder (or bottom plane) is stationary;

*Couette measuring system:* lower cylinder or bottom plane rotate; the rotational moment is measured on the inner stationary cylinder or on the top stationary plane.

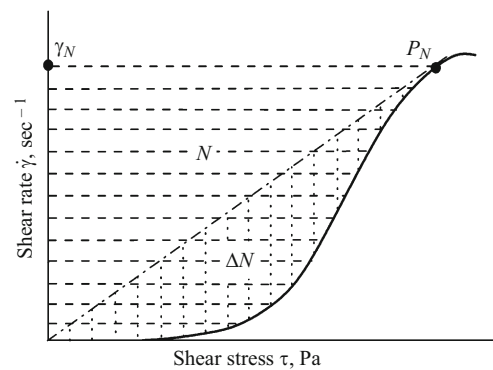
The results of the measurements on viscosimeters are friction curves or rheological curves (Fig. 7). An important advantage of rotational viscosimeters is the possibility of obtaining in a short time a complete rheological curve in a wide temperature interval, including negative temperatures. Other rheological parameters can also be measured, for example, the period of thixotropic and so one.

*Capillary Viscosimeter.* In capillary viscosimeters the measurements are performed in a nonuniform field of deformation rates [7–9, 12, 14], and the time the materials remains in the capillaries is limited. Capillary viscosimeters can be divided into two groups according to their construction:

- 1) constant pressure (the outflow time of the fluid from the capillary with a constant fluid column is measured);



**Fig. 6.** Main types of measuring cells of rotational viscosimeters: a) cylinder–cylinder; b) hemisphere–hemisphere; c) cone–cone; d) disk–disk; e) disk–ring; f) disk–cone.



**Fig. 7.** Rheological curves of thixotropic compounds.

- 2) constant flow rate (the material is pushed through a capillary at a prescribed rate and the pressure differential is measured).

On the other hand, capillary viscosimeters are divided into viscosimeters with free and forced outflow.

A drawback of free-flow viscosimeters is that the parameter values are obtained only in conditional units (for example, viscosity in Engler degrees). For this reason, forced-flow viscosimeters are used to investigate extrusion (Fig. 8) [4, 7–9, 14]. The shear rate in this case is calculated as

$$\dot{\gamma} = 4Q/(\pi R^3).$$

and the shear stress as

$$\tau = \Delta P R / (2l),$$

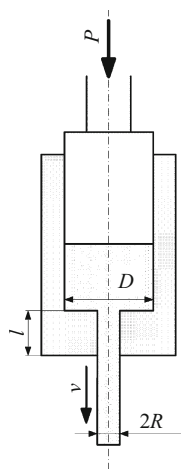
where  $Q$  is the volume flow rate;  $R$  is the radius of the capillary;  $\Delta p$  is the pressure difference; and,  $l$  is the length of the capillary.

The flow curves (see Fig. 7) can be described by the following rheological equation in a wide interval of shear rates [1–3, 7–9]:

$$\tau = \eta_0 \dot{\gamma}^n, \quad (4)$$

where  $\eta_0$  is the consistency constant,  $\text{Pa} \cdot \text{sec}^n$ , and  $n$  is the flow index.





**Fig. 8.** Scheme of the operation of an induced-flow capillary viscosimeter under a constant load.

If this equation is rewritten using Newton's law of viscous flow, we obtain Oswald's equation

$$\eta = \eta_0 \gamma^{n-1}, \quad (5)$$

The flow index in Eqs. (4) and (5) shows the degree to which the rheological behavior of the fluid deviates from Newton's law:

for  $n = 1$   $d\eta/d\tau = 0$  — ideal Newtonian fluid;

for  $n < 1$   $d\eta/d\tau < 0$  — thixotropic fluid;

for  $n > 1$   $d\eta/d\tau > 0$  — dilatant liquid.

Research has shown [1–3, 6, 14, 15, 21] that as a rule molding compounds for extrusion manifest thixotropic properties — this is a consequence of the formation of coagulation structure. As the shear stress increases, the coagulation bonds break down, which ultimately results in a transition into a Newtonian flow regime with a constant viscosity, which corresponds to the point  $P_N$  in Fig. 7. This regime is not often observed in practice, since for high rates of shear disruption of continuity and turbulence appear. The area  $N$  of the figure is the total power on the flow that is required to transfer the fluid into a Newtonian flow regime ( $W/m^3$ ); it consists of the power required for the flow itself with Newtonian viscosity and the power  $\Delta N$  required for complete destruction of the coagulation structure of the compound.

In summary, viscosimetric methods yield very valuable information about the rheological behavior of compounds. In production, there is no need to construct a complete rheological curve each time, so that to check the parameters quickly it is sufficient to measure its properties for some fixed conditions. Both capillary and rotational viscosimeters with a simplified construction [1, 13, 18], with which the rheological characteristics are obtained in arbitrary units, are used for such purposes.

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